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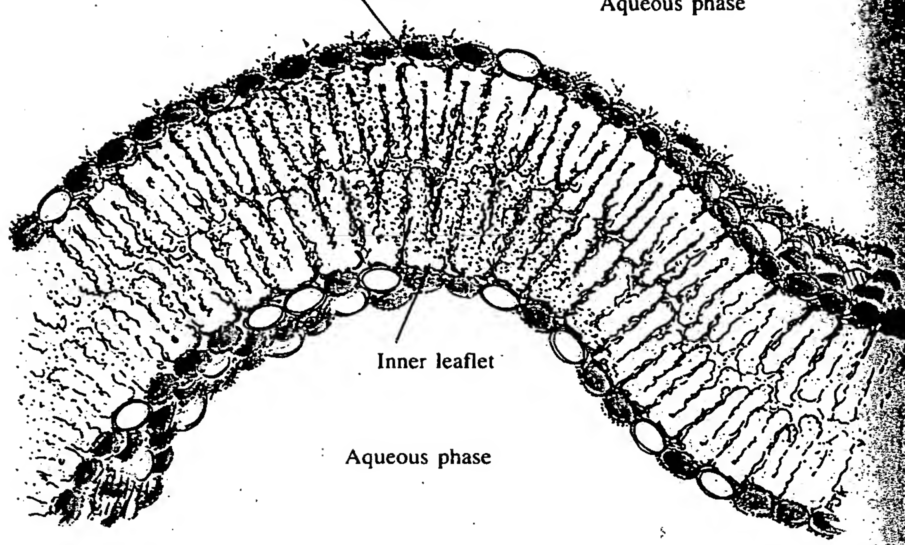

Figure 9·15
Schematic cross section of a lipid bilayer made from glycerophospholipids or sphingolipids. Polar heads extend into the aqueous medium. Nonpolar hydrocarbon tails point inward and are in van der Waals contact. (Illustrator: Florence Kabir/Advisor: Ching-hsien Huang.)

Glycerophospholipids and sphingolipids, like soaps, form monolayers, but they have an even greater tendency to do something vastly more interesting and important: they spontaneously form lipid bilayers, which are the basis of living biological membranes. The two hydrocarbon chains of these lipids are too bulky to pack well into micelles, but they fit nicely into bilayers. Unlike soap bilayers, lipid bilayers are oriented with their hydrophobic tails inside the bilayer, while the hydrophilic heads are in contact with the aqueous solution on each side (Figure 9·15). The charged polar head groups of the two layers or *leaflets* provide both surfaces with an ionic coat.

Phospholipid bilayers that enclose an aqueous compartment can be formed in high yield in the laboratory under carefully controlled conditions. These structures are called *liposomes* and can consist of a single bilayer called a unilamellar vesicle (Figure 9·16 and Stereo S9·5) or several concentric bilayers called a multilamellar vesicle. Liposomes are often employed in biochemical research because their properties resemble those of natural bilayers.

Not all lipids form bilayers. A lipid bilayer can form only when the cross-sectional areas of the hydrophobic tail and the polar head are about equal. Glycerophospholipids and sphingolipids form bilayers, but lysophospholipids, which have only one fatty acyl group, do not because the heads are too large. Likewise, cholesterol does not form bilayers because the rigid fused ring systems and additional nonpolar tails are too large.

9·7 The Hydrophobic Effect Provides the Driving Force for the Formation of Lipid Bilayers

The thermodynamic principles that govern the spontaneous assembly of lipid bilayers also control the spontaneous folding of globular proteins, the formation of nucleic acids, and the assembly of macromolecules. The generalizations we make about membrane assembly are therefore of fundamental importance.

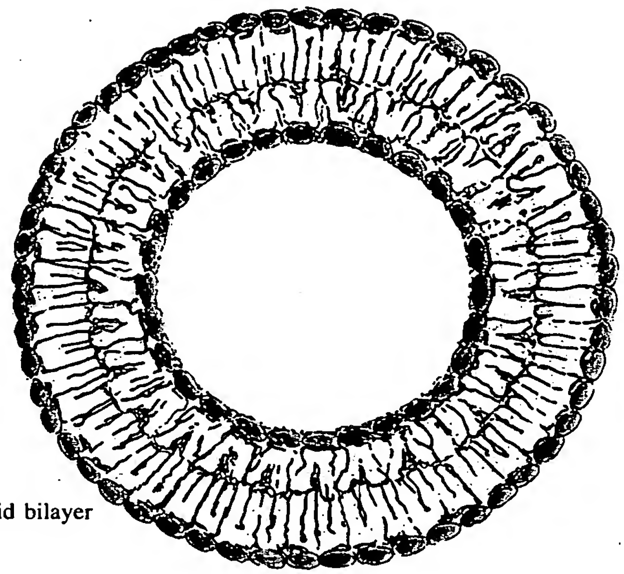

Figure 9·16
Schematic cross section of a liposome. Liposomes can be formed as unilamellar vesicles consisting of one bilayer (shown) or as multilamellar vesicles containing several concentric bilayers. (Illustrator: Florence Kabir/ Advisor: Ching-hsien Huang.)

The hydrophobic effect (Section 2·6) is the major force in the formation of lipid bilayers. Imagine a single phospholipid molecule in aqueous solution. It is surrounded by water molecules. The polar phospholipid head is highly solvated and quite stable in this state. The nonpolar tails, however, are surrounded by a structured array of hydrogen-bonded water molecules locked in a cage around the tails. These solvent molecules have little translational freedom, and therefore exist in a highly ordered, low entropy state. When the nonpolar hydrocarbon tails collect in the interior of a lipid bilayer, however, they have many van der Waals contacts with their neighbors. Furthermore, fewer water molecules are locked in a cage around the nonpolar tails; many of these water molecules have now escaped into the bulk liquid, and their translational entropy has greatly increased. The increase in solvent entropy that occurs when a phospholipid bilayer forms is greater than the decrease in phospholipid entropy (corresponding to an increase in molecular order) that results from the formation of a phospholipid bilayer. Thus, the increase in solvent entropy provides the major driving force for the formation of lipid bilayers.

Stereo S9·5
Top view of portion of the outer leaflet of a liposome, space-filling model. Polar heads extend toward the viewer and nonpolar tails extend away from the viewer. Note that phosphorus is yellow and oxygen is red. (Courtesy of Richard J. Feldmann.)